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Final Report

Contract CPA 22-69-78

FEASIBILITY STUDY OF NEW SULFUR OXIDE CONTROL PROCESSES FOR APPLICATION TO SMELTERS AND POWER PLANTS

Part I: The Monsanto Cat-Ox Process for Application to Smelter Gases

Prepared for:

U.S. DEPARTMENT OF HEALTH, EDUCATION, AND WELFARE
NATIONAL AIR POLLUTION CONTROL ADMINISTRATION
DURHAM, NORTH CAROLINA

STANFORD RESEARCH INSTITUTE
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A block flow diagram was prepared.
Mass and volume flow balances were estimated. Engineering estimates of the capital investment and the total annual cost (including both fixed and variable charges) were prepared. These engineering estimates were applied to previously created model gas streams and the total annual cost for each was determined. From these annual costs, incremental production costs were estimated. The technical constraints on the application and operation were qualitatively appraised; the economic constraints were appraised (quantitatively, to the extent permitted by the data). The current state of development was assessed, identifying any technological deficiencies whose elimination might enhance applicability.

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FOREWORD

The final report for this study is presented in four separate and independent parts:

Part I: The Monsanto Cat-Ox Process for Application to Smelter Gases

Part II: The Wellman-Lord SO_2 Recovery Process for Application to Smelter Gases

Part III: The Monsanto Cat-Ox Process for Application to Power Plant Flue Gases

Part VI: The Wellman-Lord SO_2 Recovery Process for Application to Power Plant Flue Gases

Information for use in this study was supplied to Stanford Research Institute by Monsanto Company and Wellman-Lord, Inc. under terms of confidentiality agreements between the U.S. Department of Health, Education, and Welfare, Stanford Research Institute, and each of the cooperating companies. In accordance with the agreements, Monsanto Company and Wellman-Lord, Inc. have reviewed and released the parts of the report dealing with their respective processes. The rights of prior review and release are designed solely to permit the cooperating companies to assure themselves that no proprietary or confidential data are being revealed; they are not intended to restrict Stanford Research Institute's rights and responsibilities to report its conclusions so long as there is no incidental disclosure of confidential information. Accordingly, the release of the reports by Monsanto and Wellman-Lord does not imply that these companies necessarily concur in all or any of the opinions, judgments, or interpretations of fact expressed by the author, who assumes sole responsibility for the report content.

I INTRODUCTION

Under the Systems Study for Control of Emissions -- Primary Nonferrous Smelting Industry (Contract No. PH 86-68-85), Arthur G. McKee & Company and its subcontractor, Stanford Research Institute, carried out evaluations of a number of sulfur oxide control processes as they might be applied to offgases from nonferrous smelting. To permit evaluation of the technical and economic feasibility of these control processes, a number of models of smelters were created. Stanford Research Institute carried out the studies necessary to determine the availability of markets for sulfur by-products open to smelters in various areas, and the allowable production costs that the smelters would have to attain in order to break even on the sulfur recovery operations.

The Division of Process Control Engineering of the National Air Pollution Control Administration (DPCE-NAPCA) desires to extend the usefulness of the foregoing study by adding to it technical and economic evaluations of new and potentially promising sulfur oxide control processes. It also wishes to evaluate the same new processes for application to power plants. Completion of these preliminary evaluations of the processes will help determine their potential commercial acceptability.

DPCE-NAPCA has a specific interest in at least two control processes being offered commercially, the Monsanto Cat-Ox process and the Wellman-Lord SO_2 Recovery process. However, both processes are proprietary, and, as a matter of policy, DPCE-NAPCA does not wish to obtain proprietary and confidential information on the processes. It does, nevertheless, wish to obtain evaluations in nonconfidential terms. Broadly, DPCE-NAPCA wishes to obtain estimates of the capital and annual costs of the control systems for each of the assumed applications, together with appraisals of the technical constraints on each process and of the current states of development of the processes.

Stanford Research Institute was requested by DPCE-NAPCA to carry out evaluations of the processes under the terms of confidentiality agreements between the Department of Health, Education, and Welfare, the owners of the proprietary processes, and Stanford Research Institute. SRI, acting as a disinterested third party, was to make analyses of the processes using information obtained from Monsanto Company and Wellman-Lord, Inc., and to report the results to DPCE-NAPCA without compromising any of the Monsanto or Wellman-Lord confidential data.

Because of the requirements of confidentiality, it is not permissible to describe certain features of the Cat-Ox and Wellman-Lord processes. The corresponding portions of the systems have had to be represented only in terms of their general functions, and SRI's evaluation of these portions has had to be presented in the form of conclusions without supporting data or reasoning. In other instances, the parts of the systems could be described in general, but specific details and design parameters could not be revealed.

Within the scope of the present project, it would obviously have been impossible to inspect and evaluate independently all the company records and design data even had the cooperating companies been requested to permit this and had they acceded to the request. The author of this report, who also conducted the study, evaluated the information provided at his request, using his own knowledge and relevant data from the literature and other available sources. Whenever apparent discrepancies or uncertainties were noted in the information, efforts were made to secure verification or clarification from the companies. In instances where resolution of questions was not possible, or the information required proved to be simply unavailable, the author employed his best judgment.

Throughout the following sections of this report, information for which other sources are not specifically cited was generally obtained from the cooperating companies and accepted by the author either because it could be verified from other sources or because it appeared reasonable. In other instances, information or estimates were provided by the companies

that could not be verified independently or judged for reasonableness; in such cases, the companies have been specifically cited as the sources. In still other instances, the author did not accept the information or estimates provided and in some cases substituted his own; such cases have also been specifically noted.

The cooperating companies, at their own option and through substantial efforts, provided the basic capital cost estimates for the model control systems and the information for estimation of operating and maintenance costs. The author in this case acted as a reviewer rather than as an estimator. The estimates were checked for reasonableness and for possible errors or omissions. For some components and cost factors, the author modified the estimates, or substituted others of his own where he judged them to be more appropriate than those supplied to him. The author also prepared cost estimates for some auxiliary systems, using separate data sources.

By specification of the power plant and smelter models, and by review of the results, an effort was made to ensure that the cost estimates for both control systems were made on strictly comparable bases. Although it is unlikely that this objective has been met fully, the deviations are probably within the precision of the estimates themselves.

For convenience, and at the request of DPCE-NAPCA, this final report is presented in four separate and independent parts. This part deals only with the Monsanto Cat-Ox process as applied to control of sulfur oxides in the offgases from copper, lead, and zinc smelters.

II OBJECTIVES

The objectives of the part of the study covered by this report are as follows:

1. To prepare a block flow diagram of the Cat-Ox system showing its configuration and its relation to the smelting processes in which the sulfur oxides are generated.

2. To present estimated mass and volume flow balances for the Cat-Ox system.

3. To prepare preliminary engineering estimates of the capital investment and the total annual cost (including both fixed and variable charges) for the Cat-Ox system.

4. To apply the estimates prepared in (3) to the gas streams of the model smelters created in the previous Systems Study for Control of Emissions -- Primary Nonferrous Smelting Industry, and to determine the total annual cost for each model control system. From the estimates of total annual costs, secondary estimates are to be made of the corresponding incremental costs of producing the nonferrous metals, both on the gross basis (without allowance for by-product recovery credits) and on the net basis (with allowance for by-product recovery credits).

5. To make a qualitative appraisal of technical constraints on the application and operation of the control system.

6. To appraise (quantitatively, to the extent permitted by available data) the economic constraints on the application of the control system.

7. To assess the current state of development of the Cat-Ox system, identifying any technological deficiencies whose elimination might enhance the applicability of the system to smelter gases.

The accomplishment of the objectives is subject to any restrictions that may be imposed under the terms of the confidentiality agreement between the Government, Monsanto Company, and Stanford Research Institute.

III SUMMARY

The Monsanto Cat-Ox system for sulfur oxides recovery is essentially an adaptation of the well-known contact process for sulfuric acid manufacture. The gas containing both sulfur dioxide and oxygen is passed through a fixed bed of catalyst at an appropriate temperature and most of the sulfur dioxide is oxidized to sulfur trioxide. The gas is then passed through an absorption tower where the sulfur trioxide is absorbed in recirculated sulfuric acid. The Cat-Ox system has been developed primarily for use on power plant flue gases, but it is also adaptable to other dilute gas streams -- such as smelter gases -- that contain about 2 percent or less of sulfur dioxide. It differs from the conventional contact process plant in three principal respects:

1. The feed gas entering the system either must be already at a temperature high enough for conversion of the sulfur dioxide to the trioxide in the catalytic converter, or else auxiliary heat must be supplied to raise the temperature. Because of the diluteness of the sulfur dioxide, the plant is not autothermal; that is, the heat released by the oxidation of the sulfur dioxide is insufficient to preheat the feed gas to the reaction temperature.

2. The system operates on wet gas. The feed gas is not dried before it enters the converter.

3. The heat in the exit gas is used to a greater or lesser degree to concentrate the sulfuric acid formed in the final absorption step.

The version of the Cat-Ox process proposed for use on smelter gases is similar to the "Cat-Ox reheat system" proposed for application to existing power plants (see Part III of Final Report for this study). The feed gas must be preheated before entering the converter. Part of the preheating is accomplished by transfer of heat from the hot gas leaving the converter; the rest is supplied by an indirect gas-fired heater. The partly cooled converter exit gas enters the absorption system where the

sulfur trioxide is absorbed. If the concentration of the acid produced is to be about 78 percent, the absorption system will consist of a single absorption tower as in the power plant control systems. If 93-percent acid is to be produced, as is specified in this study, additional equipment and a more complicated arrangement must be used.

In smelter applications of the Cat-Ox process, it is practical to concentrate the acid to 93 percent because the heat required is already available in the exit gas and there is little other possible use for it. Although the same thing could be done in the Cat-Ox reheat system for power plants, the cost would be relatively much greater because of the lower concentration of sulfur oxides; use of a separate, conventional acid concentrator should be preferable with respect to both capital and operating costs. In the integrated Cat-Ox system for power plants, heat taken for concentration of the acid would be lost to the power generation cycle.

Because the gas is not dried before conversion of the sulfur dioxide to sulfur trioxide, the amount of sulfuric acid mist formed during the gas cooling and absorption steps is relatively much higher than that formed in the conventional contact process. Hence, a high-efficiency mist collector must be used to recover the mist from the tail gas. In the Cat-Ox process, a fiber-bed mist eliminator is employed.

Contaminants (dust and fumes, vapors, and gases) in the feed gas present the same problems in the Cat-Ox system for smelters as they do in conventional contact process plants. It was therefore specified by SRI as a model condition that the gas should be assumed to be cleaned to the same degree as it would be for use in a contact process plant. It is reasonable to expect that the residual contaminants in the clean gas should produce no more problems in a Cat-Ox plant than they would in a conventional contact plant.

All the basic concepts of the Cat-Ox process have been demonstrated previously, and a process similar to the smelter-gas version of the Cat-Ox system has been in commercial operation in Europe for a number of

years. The Cat-Ox system is not, in principle, restricted to use on dilute gas streams, but it offers no advantages over the contact process for use on rich gases. The principal limitations on its application to smelter gases appear to be economic rather than technical. The recovery of sulfur dioxide from dilute gas streams is inherently expensive, regardless of the process used. In addition, sulfuric acid is not a desirable by-product in the geographical areas of the United States where the largest number of applications of the Cat-Ox process to smelters might be made. The markets for acid are limited, and they can be more economically supplied from plants operating on richer gases.

In the model studies using the smelter models created by Arthur G. McKee & Company, the Cat-Ox process was applied only to gas streams containing 2 percent or less of sulfur dioxide. The results are summarized in Table I, which presents the gross production cost for sulfuric acid (100-percent basis) and the gross incremental cost of producing the metals, before allowance of credits for sale of the 93-percent product acid. Even with the richest of the gases, containing approximately 2 percent of sulfur dioxide, the acid production cost exceeded $11/ton, which would make the acid noncompetitive with that from alternative available sources (such as rich smelter gases) in such areas as Montana-Idaho and Arizona-New Mexico-West Texas. For gases containing less than 2 percent of sulfur dioxide, the acid production cost rose rapidly with decrease in the sulfur dioxide concentration. Plant size was an additional but much less important factor in the determination of the acid production cost.

For the copper reverberatory furnaces, the gross incremental cost of producing copper (without by-product credit) ranged from 0.4 to 0.8 cent/lb, depending upon sulfur dioxide concentration and plant size. For the model zinc smelters, the gross incremental cost of producing zinc, resulting from control of sulfur oxide emissions in dilute gases, ranged from 0.9 to 2.6 cents/lb. These incremental costs would be reduced relatively little by any by-product credits likely to be realizable. However, in the case of copper, the gross incremental cost is a small fraction of the current

Table I

SUMMARY OF ESTIMATED COSTS
CAT-OX SYSTEMS APPLIED TO MODEL SMELTERS

Model Smelter	Gas Stream	SO_2 Concentration (%)	Gross Acid Production Cost ($/ton)[1]	Gross Incremental Cost of Metal Production (¢/lb)[2]
Copper				
Model A	Reverberatory Furnace	1.89		
	Small		15.54	0.84
	Medium		12.62	0.67
	Large		11.37	0.61
Model B	Reverberatory Furnace	0.91		
	Small		38.28	0.59
	Medium		30.29	0.47
	Large		27.00	0.42
Zinc				
Model B	Roaster	0.9	26.82	1.75
	Sinter Plant	0.5	69.18	0.86
Model C	Roaster	0.8	25.89	1.97
Model D	Sinter-Roaster	2.0	11.75	0.92

[1] Includes both fixed and variable charges. See Appendix B for bases.

[2] Before allowance for by-product acid credit.

price of copper, or even of the increase in the price of copper that has taken place in the period 1969-1970. On the other hand, the incremental costs for production of zinc are larger not only absolutely but also in relation to zinc prices.

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IV PROCEDURES

A. Models

The models of the hypothetical smelters, which are presented in Appendix A, are the same as those formulated and used in the previous study of smelter emission control by Arthur G. McKee & Company.[9] Some supplemental conditions, necessary to the specific analyses of the Cat-Ox and Wellman-Lord processes, were specified by SRI and are also given in Appendix A.

B. Cost Factors

The factors used in making the cost estimates for the control systems were also taken from the McKee report,[9] and are presented in Appendix B. Some supplemental factors needed specifically for the present study were specified by SRI.

The estimates of the prices that might be obtained for sulfur by-products were also taken from the McKee report.[9]

C. Preparation of Technical Data and Cost Estimates

The Monsanto Company prepared the technical designs for the model control systems, based on the model conditions specified by SRI, and estimated the capital investments and the utility and maintenance requirements. In making the estimates, Monsanto used as its basis a relatively detailed cost estimate that it had made for a proposed Cat-Ox plant for an actual smelter. They estimated the capital costs for the ten hypothetical installations individually by applying appropriate ratios to the costs of the component parts of the base-case plant. The author reviewed the estimates, but since the design data and specific component configurations were in most cases not revealed by Monsanto, it was generally impractical to make a critical, independent analysis

of the capital cost estimates. The cost breakdowns for individual major components of some of the systems were supplied by Monsanto, however, and were surveyed only for general reasonableness and consistency with the model specifications.

Because the original cost estimates made by Monsanto for the base-case plant were made on the basis of assumptions somewhat different from those used in the present study, the capital and operating cost estimates for the ten hypothetical installations had to be modified. The modifications of the estimates were made by the author after obtaining additional information from, and reviewing proposed changes with, Monsanto Company.

The cost estimates for the gas cleaning system used ahead of the Cat-Ox system were prepared by the author (see Appendix C).

V PROCESS DESCRIPTION

The Monsanto Cat-Ox process is essentially a variation on the contact process for sulfuric acid manufacture, which is extensively treated in the literature.[4] The process was developed primarily for removal of sulfur dioxide from the flue gases of coal- or oil-fired power plants[10, 13,14,15] in which the sulfur dioxide concentration usually falls within the range from 0.1 to 0.4 percent by volume, but it can be used on richer gases. It differs from the conventional contact process in three principal respects:

1. Because of the diluteness of the sulfur dioxide, the plant is not autothermal; that is, the heat released by the oxidation of the sulfur dioxide is insufficient to preheat the feed gas to the reaction temperature (generally above 800°F). Hence, if the gas is not already near that temperature, auxiliary heat must be employed.

2. The system operates on wet gas. The feed gas is not dried before it enters the converter (catalytic reactor). Hence, the amount of sulfuric acid mist formed is relatively much greater than that formed in the conventional contact process, and a collector must be employed to recover the mist from the tail gas.

3. The heat in the exit gas from the converter is used to a greater or lesser degree to concentrate the sulfuric acid formed in the final absorption step. The concentration of the acid produced depends upon the temperature to which the flue gas stream is reduced during contact with the acid in the absorber.[14]

All of the component basic concepts of the Cat-Ox system have been demonstrated previously under some circumstances. Catalytic oxidation of sulfur dioxide at low concentrations has been demonstrated previously in the laboratory[12] and in pilot plant studies that were preliminary parts of the development of the Cat-Ox system.[15] A similar process (SNPA-Topsoe) has been in large-scale commercial operation at Lacq, France for several years on the incinerated tail gases from a Claus sulfur plant;[5,6,7]

there the concentration of sulfur dioxide is of the order of 1.0 percent, and a two-stage absorption process is used to produce 94-percent acid.

Some relatively conventional contact plants for manufacture of sulfuric acid from hydrogen sulfide have been built for use on wet gases.[4] The hot gas from the combustion of hydrogen sulfide (partly cooled in a waste heat boiler and diluted with air to give a sulfur dioxide concentration of about 7.5 percent) enters the converter without being dried. The hot exit gas from the converter is not cooled, as is customary in contact plants, but goes directly to an absorber. Because of the relatively high water content of the gas stream, it is not feasible to produce acid stronger than 93 to 94 percent. Also, relatively large quantities of sulfuric acid mist are formed that must be removed from the tail gas with some type of mist collector. The principal advantage sought in this type of plant is a reduction in capital cost.

This report treats a variation of the Cat-Ox process proposed for application to smelter gases (Fig. 1), which is essentially similar to the Cat-Ox reheat system[11] intended for application to existing power plants. The system treated is a conceptual design; no pilot or commercial plant has been constructed and tested. However, as noted above, components of the system have, in one way or another, been tested elsewhere.

The Cat-Ox system shown in Fig. 1 is designed for use on gases containing 2 percent or less of sulfur dioxide. In principle, the Cat-Ox process is applicable to rich as well as lean gases. As applied to rich gases, it would be very similar to the wet-gas plants designed for use on the gases from combustion of hydrogen sulfide, which are described above and in the literature.[4] However, preliminary discussions between Monsanto and SRI representatives gave indications that, for use on rich smelter gases, the Cat-Ox process would have no substantial advantages over the conventional contact process and might suffer some additional penalties. Hence, no estimates were made for Cat-Ox plants to handle gases containing more than 2 percent of sulfur dioxide.

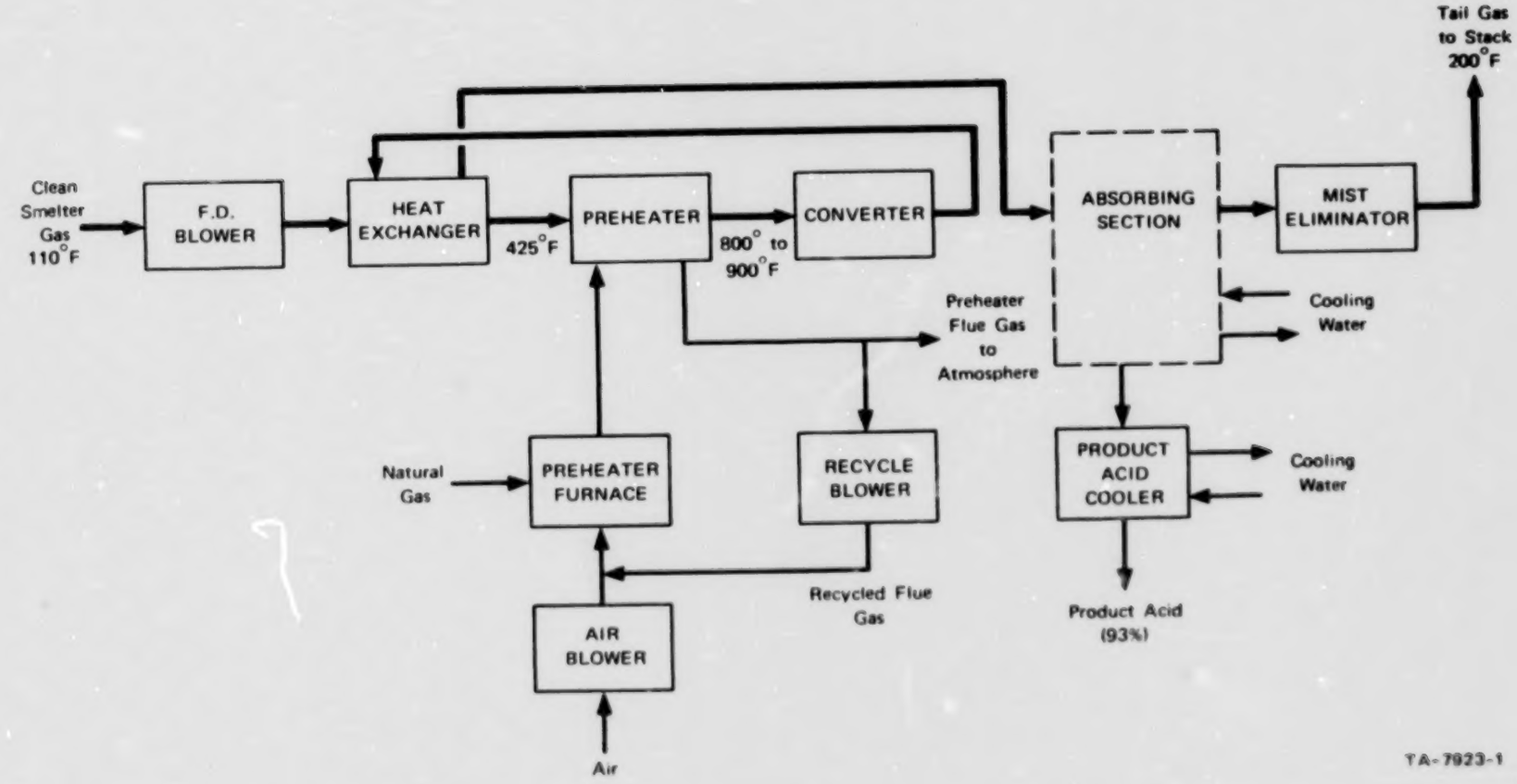

FIGURE 1 CAT-OX SYSTEM FOR SMELTER GASES

When used on smelter gases, the Cat-Ox process is subject to the same potential problems from contaminated feed gas as is the conventional contact process -- catalyst-bed plugging, catalyst poisoning, and corrosion. However, it can reasonably be assumed that if the feed gas is purified to the degree acceptable for use in contact plants, the residual contaminants should produce no more problems in a Cat-Ox plant than in a standard contact plant. Monsanto has prepared conceptual designs for smelter gas Cat-Ox plants based on the assumption that the gases contained more inert solids than are normally acceptable in contact plants, but that no excessive quantities of catalyst poisons or corrosive materials (such as lead and zinc oxides, fluorides, chloride, and arsenic) were present. For the present study, SRI specified that the smelter gas entering the Cat-Ox system should be assumed to: (1) have been purified in a gas cleaning system typical of those used with contact sulfuric acid plants, (2) contain residual contaminants in concentrations at least as low as are specified by Donovan and Stuber[3] for acceptability in contact plants, and (3) be at 110°F and saturated with water vapor. The capital and operating costs of the gas purification system are charged against sulfur oxide recovery, but were estimated separately by SRI from literature data (see Appendix C and Section VI) and are presented as separate items.

The clean, cold gas from the gas cleaning system enters a blower (Fig. 1) that forces the gas through the Cat-Ox system. From the blower the gas goes first to the heat exchanger where it is partly heated by the hot exit gas from the converter, then to the natural-gas-fired preheater where it is raised to a suitable temperature (in the range of 800 to 900°F) for catalytic oxidation of the sulfur dioxide in the converter.

The system is designed to give an exit concentration of sulfur dioxide not exceeding 500 parts per million with inlet concentrations of up to 2.0 percent. The converter is therefore designed for higher conversions than are the converters for the power plant units. With the richer smelter gas streams, the heat released in the oxidation of the sulfur dioxide is sufficient to raise the temperature of the gas to levels that may require control. The design features used to provide for the desired conversion

and for gas temperature control are based on established principles and techniques but are not shown in Fig. 1 or described here, because Monsanto does not wish to disclose the particular approaches used.

After being partly cooled in the heat exchanger, the converter exit gas enters the absorption section of the plant, where product acid is recovered. The acid recovered may be either relatively weak (78 percent, for example) or strong (93 percent). The absorption system for production of the weak acids is essentially identical to that used in the power plant Cat-Ox system.[10,11] Producing the strong acid requires more equipment and a more complicated system. This latter system is not shown in Fig. 1 or described here because Monsanto does not wish to make a public disclosure of the specific method used. The system is, however, a feasible one that has been anticipated in the prior art.

After leaving the absorption system, the gas passes through a Brink[1] or Cat-Ox[11] mist eliminator, where the residual sulfuric acid mist and entrained acid droplets are removed.

In the gas-to-gas heat exchanger of the Cat-Ox system, cold-end corrosion must be avoided as it must be also in the similar exchangers of the power plant control systems. In the smelter gas plant, corrosion is prevented by the use of cocurrent instead of counter-current flow of the cold and hot gases, but at the expense of reduced heat recovery from the hot gas stream.

In the smelter gas Cat-Ox system, as in conventional contact acid plants, the economic balance generally favors incurring relatively high power costs in order to reduce capital investment. Consequently, the converter is designed to use relatively deep catalyst beds and high gas velocities while minimizing unit size. The pressure drop across the clean converter is 27 inches of water, and that through the entire system (when clean) is approximately 85 to 90 inches. Allowance is made for an additional 60 inches of water pressure drop due to dirt buildup.

With the feed gas cleaned to the specified degree, it is anticipated that it will not be necessary to remove and clean the catalyst, or clean

the mist eliminator, more than once per year. This maintenance work can be accomplished during the annual shutdown. Monsanto estimates the loss of catalyst during a single cleaning operation at 5 percent, on the basis of experience with conventional contact acid plants.

The production of 93-percent sulfuric acid was specified by SRI. Weaker acid could be produced, as noted above, in a simpler and less expensive absorption system. However, this modification would apparently reduce the capital investment by no more than 5 to 6 percent and also would not reduce the operating cost by any substantial fraction. The weak acid would be salable only under special circumstances. Previous market studies[9] have shown that markets for even strong acid are limited in precisely those areas where there are the greatest potential applications of the Cat-Ox process to smelter gases (see Section VII).

Dry, hot cleaning of the smelter gas fed to the Cat-Ox unit would not necessarily result in major savings even if it were undertaken on the hazardous assumption that no volatile or gaseous contaminants (such as fluorides, chlorides, and arsenic) are present. Current, conventional hot electrostatic precipitator installations could probably be expected to allow passage of at least five to ten times the amount of dust that would penetrate the combination wet cleaning system (see Appendix C). The amount of catalyst cleaning and catalyst loss would be increased proportionately, as would be the maintenance required on the mist eliminator. The necessity for auxiliary heat would remain, since all of the smelter gas streams are (at least once they have been cooled to permit dry cleaning) still at temperatures below those required for operation of the converter, which are generally above 800°F. Many dilute smelter gas streams are at temperatures in the range of 200 to 500°F.[9]

VI PROCESS DATA AND COST ESTIMATES

A. Sulfur Oxides Recovery

In the smelter models (Appendix A) the distribution of the emitted sulfur oxides between sulfur dioxide and sulfur trioxide is in most cases not given. Where the concentration of sulfur trioxide in the gas is not specified, the concentration of sulfur dioxide is calculated on the assumption that all of the sulfur is in the form of sulfur dioxide (see Table A-1). In fact, a variable quantity of sulfur trioxide (equivalent to a few percent of the total sulfur emission) will be present in all cases, and will be removed in the gas cleaning system that precedes the sulfur dioxide recovery system. However, for the sake of simplification, it was assumed in this study that all of the sulfur was in the form of sulfur dioxide and was treated in the sulfur dioxide control system. The inputs and outputs of sulfur from the recovery systems were calculated on this basis.

In the McKee study,[9] different collection efficiencies for sulfur dioxide were assumed for the various control systems modeled, as appeared appropriate for the systems considered. In the present study, a uniform standard of performance was set for both of the recovery systems (Cat-Ox and Wellman-Lord) that were treated (see Appendix A). Both systems appeared to be capable of attaining or exceeding the efficiencies specified, at least within the ranges of input sulfur dioxide concentrations for which their application was appropriate. The calculated collections of sulfur dioxide and yields of by-products for the model plants were based on attainment of the specified efficiencies.

B. Gas Cleaning

The costs (capital and operating) of preliminary gas cleaning (see Appendix C) were taken to be the same for both the Cat-Ox and Wellman-Lord

systems. However, the costs for the gas cleaning and sulfur dioxide recovery systems are presented separately in this report, and are combined only in final totals.

The capital cost for the gas cleaning system does not include that for the fan, which is assigned to the sulfur dioxide recovery system. However, the operating cost for the gas cleaning system does include the cost of electrical power consumed by the fan that moves the gas through the gas cleaning system.

The maximum allowable concentrations of impurities in the cleaned gas (Appendix A and Reference 3) are apparently higher, in at least a few instances, than the levels that are favored by some other authorities or that are attained in some installations. For sulfuric acid mist, Donovan and Stuber[3] give an upper limit of 0.022 grain/std cu ft, which is assumed in this study, whereas Carter[2] favors a maximum of 0.0012 grain/cu ft. Heinrich and Anderson[8] report attainment of residual acid mist and arsenic concentrations as low as 0.0000022 grain/cu ft with a wet electrostatic precipitator.

C. Operating Requirements for Cat-Ox Systems

The factors used to calculate the materials, utilities, and labor required for the various model control systems are summarized in Table II. They are based on information obtained from Monsanto Company. The cost of catalyst makeup is based on cleaning the catalyst once per year, with an attendant loss of 5 percent.

D. Cost Estimates

The gas flow rates and the annual sulfuric acid production rates for the model Cat-Ox systems are presented in Table III. The capital and total annual costs for the model Cat-Ox systems, alone, are presented in Table IV. In Table V, the summarized capital and annual costs of both the gas cleaning and Cat-Ox systems are presented separately and then added to give the total costs for the complete sulfur dioxide recovery systems. Table V also shows the contributions of both parts of the systems

Table II

CAT-OX SYSTEMS FOR SMELTER GASES
REQUIREMENTS FOR MATERIALS, UTILITIES, AND LABOR

Catalyst Makeup

Annual cost = $0.105 per SCFM of gas rate

Makeup Cooling Water

5.66 gpm per 1000 SCFM of gas rate

Electrical Power

440 kwh per day per 1000 kwh SCFM of gas rate

Natural Gas

1162 CFH per 1000 SCFM of gas rate

Labor[1]

3 men per shift = 72 man-hours per day

Supervision[1]

2 man-hours per shift = 6 man-hours per day

[1] Estimates of labor and supervision based on experience with conventional contact acid plants.

Table III

GAS FLOW RATES AND SULFURIC ACID PRODUCTION RATES FOR CAT-OX SYSTEMS

Model Smelter	Gas Flow Rate ACFM ($110^{o}F$, 1 atm, sat'd)	Sulfuric Acid Production tons/year (100% basis)
Copper Model A		
Reverberatory Furnaces		
Small	81,000	81,180
Medium	162,000	162,360
Large	243,000	243,540
Copper Model B		
Reverberatory Furnaces		
Small	48,800	23,500
Medium	97,700	47,190
Large	146,600	70,620
Zinc Model B		
Roaster	154,400	73,590
Sinter Plant	55,500	14,030
Zinc Model C		
Roaster	409,600	172,260
Zinc Model D		
Sinter-Roaster	166,900	177,870

Table IV

CAT-OX SYSTEMS FOR SMELTER GASES
CAPITAL AND ANNUAL COSTS FOR CAT-OX SYSTEMS ONLY[1]

Item	Copper Model A Reverberatory Furnaces			Copper Model B Reverberatory Furnaces			Zinc Model B		Zinc Model C	Zinc Model D
	Small	Medium	Large	Small	Medium	Large	Roaster	Sinter Plant	Roaster	Sinter-Roaster
Capital Investment ($)	2,460,000	3,760,000	4,820,000	1,691,000	2,731,000	3,570,000	3,650,000	1,817,000	8,620,000	3,815,000
Annual Cost ($)										
A. Depreciation	164,000	250,670	321,335	112,735	182,070	238,000	243,335	121,135	574,670	254,335
B. Direct Operating Cost										
1. Labor	89,100	89,100	89,100	89,100	89,100	89,100	89,100	89,100	89,100	89,100
2. Supervision	9,405	9,405	9,405	9,405	9,405	9,405	9,405	9,405	9,405	9,405
3. Payroll benefits	24,630	24,630	24,630	24,630	24,630	24,630	24,630	24,630	24,630	24,630
4. Maintenance materials	73,800	112,800	144,600	50,730	81,930	107,100	109,500	54,510	258,600	114,450
5. Factory supplies	12,300	18,800	24,100	8,460	13,660	17,850	18,250	9,090	43,100	19,080
6. Catalyst makeup	7,340	14,680	22,020	4,425	8,850	13,280	13,990	5,030	37,110	15,120
7. Electricity	101,500	203,000	304,500	61,200	122,400	183,700	193,400	69,600	513,200	209,100
8. Natural gas	257,320	514,800	772,000	155,160	310,320	465,600	490,400	176,320	1,301,200	530,000
9. Cooling water makeup	3,760	7,520	11,280	2,280	4,540	6,800	7,160	2,580	19,000	7,740
C. Indirect Costs										
1. Controllable	86,150	105,650	121,550	74,620	90,220	102,800	104,000	76,150	178,550	106,480
2. Noncontrollable	73,800	112,800	144,600	50,730	81,930	107,100	109,500	54,510	258,600	114,450
Total Annual Cost ($) (Gross)	903,105	1,463,855	1,989,120	643,475	1,019,055	1,365,365	1,412,670	692,060	3,307,165	1,493,990

[1] Not including gas cleaning systems.

Table V

CAT-OX SYSTEMS FOR SMELTER GASES
CAPITAL AND OPERATING COSTS FOR CAT-OX AND GAS CLEANING SYSTEMS

	Copper Model A Reverberatory Furnaces			Copper Model B Reverberatory Furnaces			Zinc Model B		Zinc Model C	Zinc Model D
	Small	Medium	Large	Small	Medium	Large	Roaster	Sinter Plant	Roaster	Sinter-Roaster
Capital Investment ($)										
Gas Cleaning System	1,830,000	2,950,000	3,900,000	1,280,000	2,080,000	2,750,000	2,850,000	1,410,000	5,550,000	3,000,000
Cat-Ox System	2,460,000	3,760,000	4,820,000	1,691,000	2,731,000	3,570,000	3,650,000	1,817,000	8,620,000	3,815,000
Total	4,290,000	6,710,000	8,720,000	2,971,000	4,811,000	6,320,000	6,500,000	3,227,000	14,170,000	6,815,000
Annual Cost ($)										
Gas Cleaning System	358,000	583,000	780,000	256,000	408,000	540,000	560,000	278,000	1,150,000	595,000
Cat-Ox System	903,000	1,464,000	1,989,000	643,000	1,019,000	1,365,000	1,413,000	692,000	3,307,000	1,494,000
Total	1,261,000	2,047,000	2,769,000	899,000	1,427,000	1,905,000	1,973,000	970,000	4,457,000	2,089,000
Acid Production Cost ($/ton 100% acid)										
Gas Cleaning System	4.41	3.59	3.20	10.89	8.65	7.65	7.61	19.82	6.68	3.35
Cat-Ox System	11.13	9.03	8.17	27.39	21.64	19.35	19.21	49.36	19.21	8.40
Total	15.54	12.62	11.37	38.28	30.29	27.00	26.82	69.18	25.89	11.75
Gross Cost per Unit Quantity of Metal Produced[1] (¢/lb)										
Gas Cleaning System	0.24	0.19	0.17	0.17	0.13	0.12	0.50	0.25	0.51	0.26
Cat-Ox System	0.60	0.48	0.44	0.42	0.34	0.30	1.25	0.61	1.46	0.66
Total	0.84	0.67	0.61	0.59	0.47	0.42	1.75	0.86	1.97	0.92

[1] Before allowance for by-product credits.

to the total acid production costs and to the total gross incremental costs of producing metal.

The capital and total annual costs of the gas cleaning systems and Cat-Ox systems and the combinations of the two are shown graphically in Figs. 2 and 3. The data points from which the cost curves were constructed were taken from Table V. It can be seen that the estimated capital cost of the Cat-Ox system is not a function of the sulfur dioxide concentration, at least over the range of concentrations considered (0.5 to 2.0 percent). The relationship of capital cost to system gas-handling capacity is, however, affected by the size of the installation. In the largest plant (410,000 CFM at 110°F and 1 atm), some of the components in the system are composed of multiple units, which increases the ratio of cost to capacity. It appears that for plants larger than about 400,000 CFM capacity, the capital costs will be about proportional to capacity. However, in plants of up to about 250,000 CFM capacity, the capital cost is proportional only to about the 0.6 power of capacity.

The annual costs of the Cat-Ox system (Fig. 3) reflect the capital costs, but are essentially independent of sulfur dioxide concentration. Hence, the unit costs of producing sulfuric acid are decreased appreciably by increase in plant size, but are radically increased by decreases in the sulfur dioxide concentration.

In Figs. 4 through 6 the changes in the unit production costs of the metals, resulting from the application of Cat-Ox systems to the various model smelters, are shown graphically as functions of the net selling price of the product acid at the smelter. The net selling price is equal to the gross selling price less sales cost and overhead, and will, of course, be dependent upon the particular location of the plant. As is noted below (see Section VII), it is unlikely that at most locations it would be possible to realize sufficient return from the sale of acid to offset a substantial part of the gross incremental cost of producing the metal. The model smelters that have the best opportunities are the Model A copper smelters and the Model D zinc smelter, which have the richest gases (about 2 percent of sulfur dioxide).

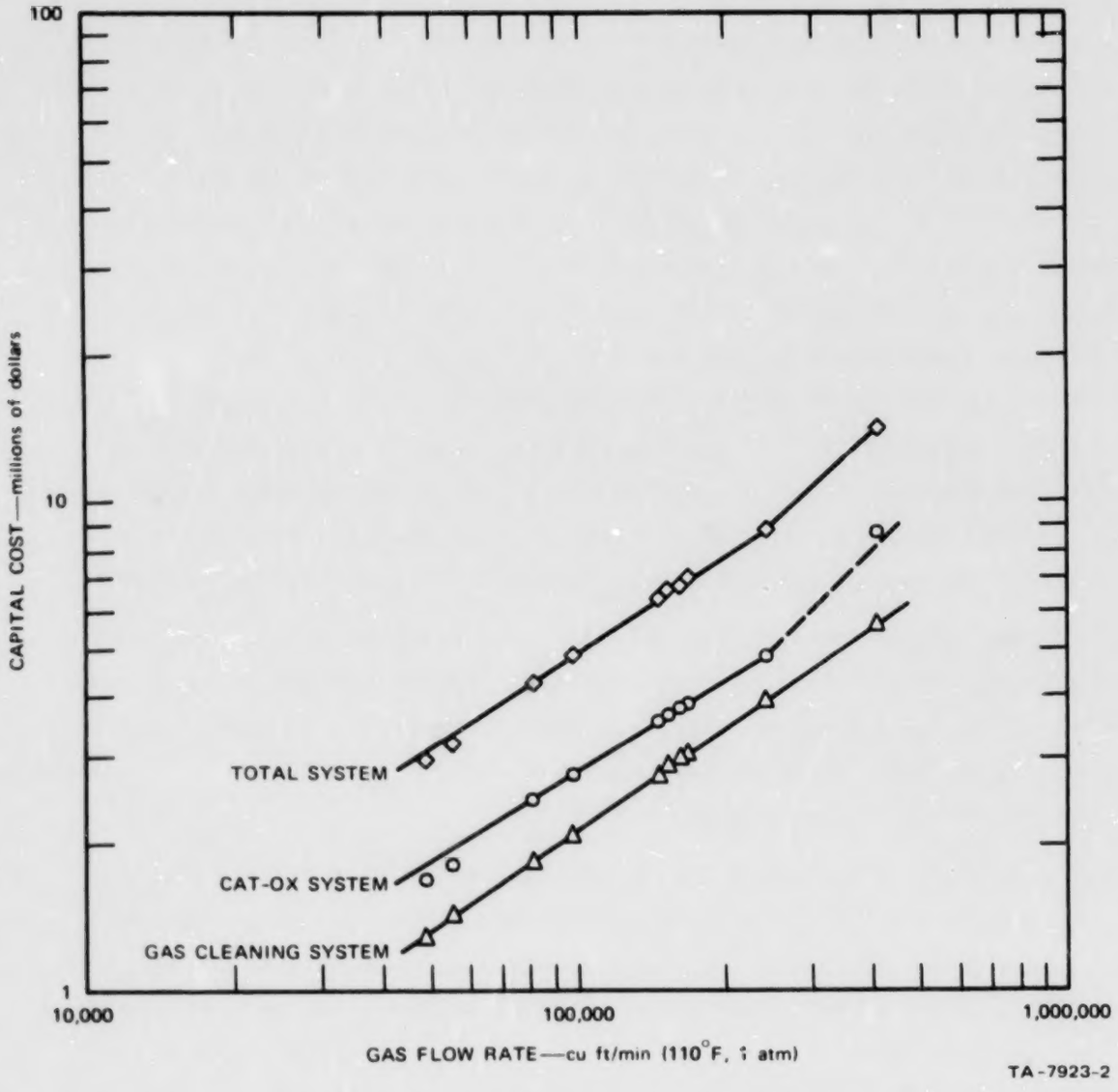

FIGURE 2 CAPITAL COSTS OF CAT-OX AND GAS CLEANING SYSTEMS FOR SMELTER GASES

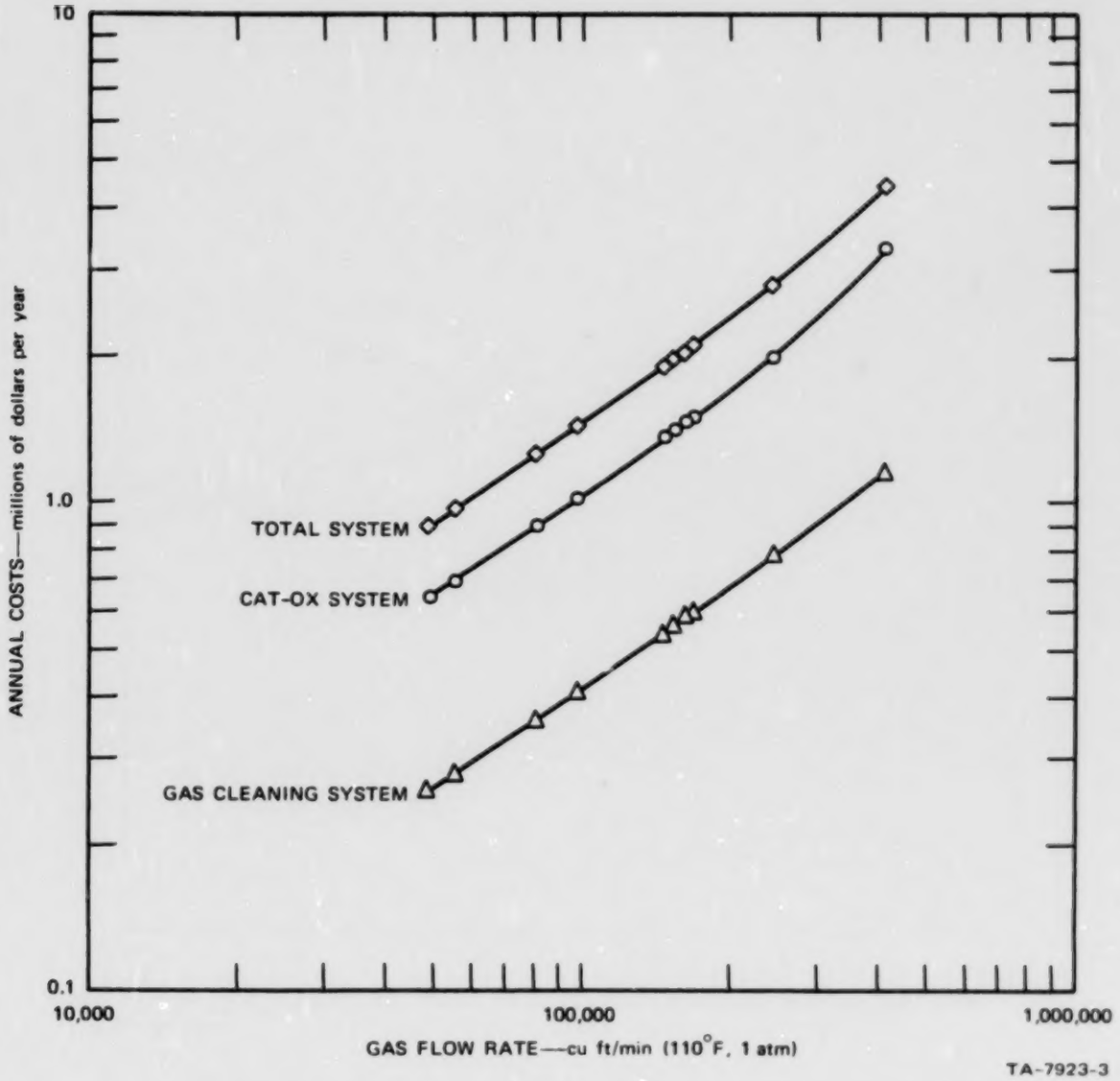

FIGURE 3 ANNUAL COSTS OF CAT-OX AND GAS CLEANING SYSTEMS FOR SMELTER GASES

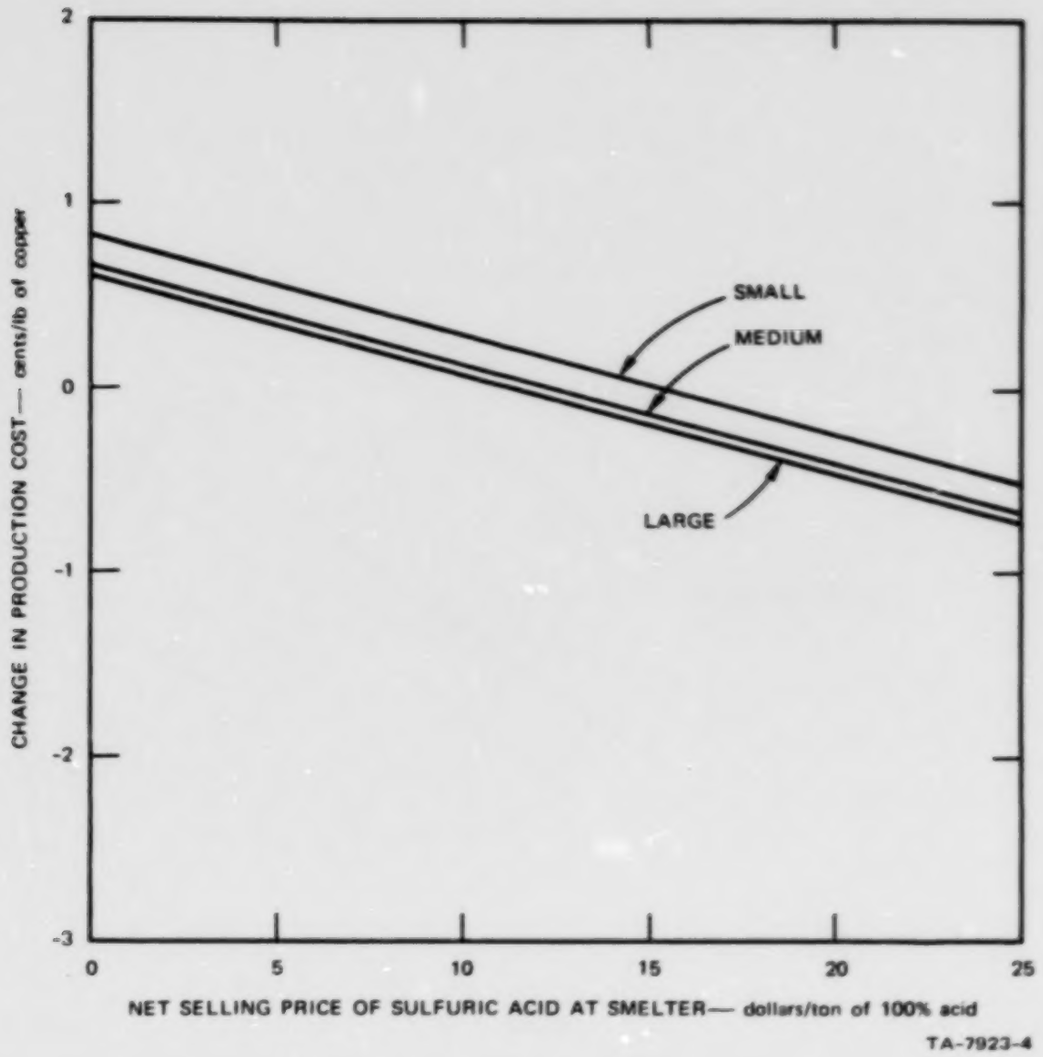

FIGURE 4 MODEL A COPPER SMELTERS: CAT-OX SYSTEMS ON REVERBERATORY FURNACES—EFFECT ON COPPER PRODUCTION COSTS

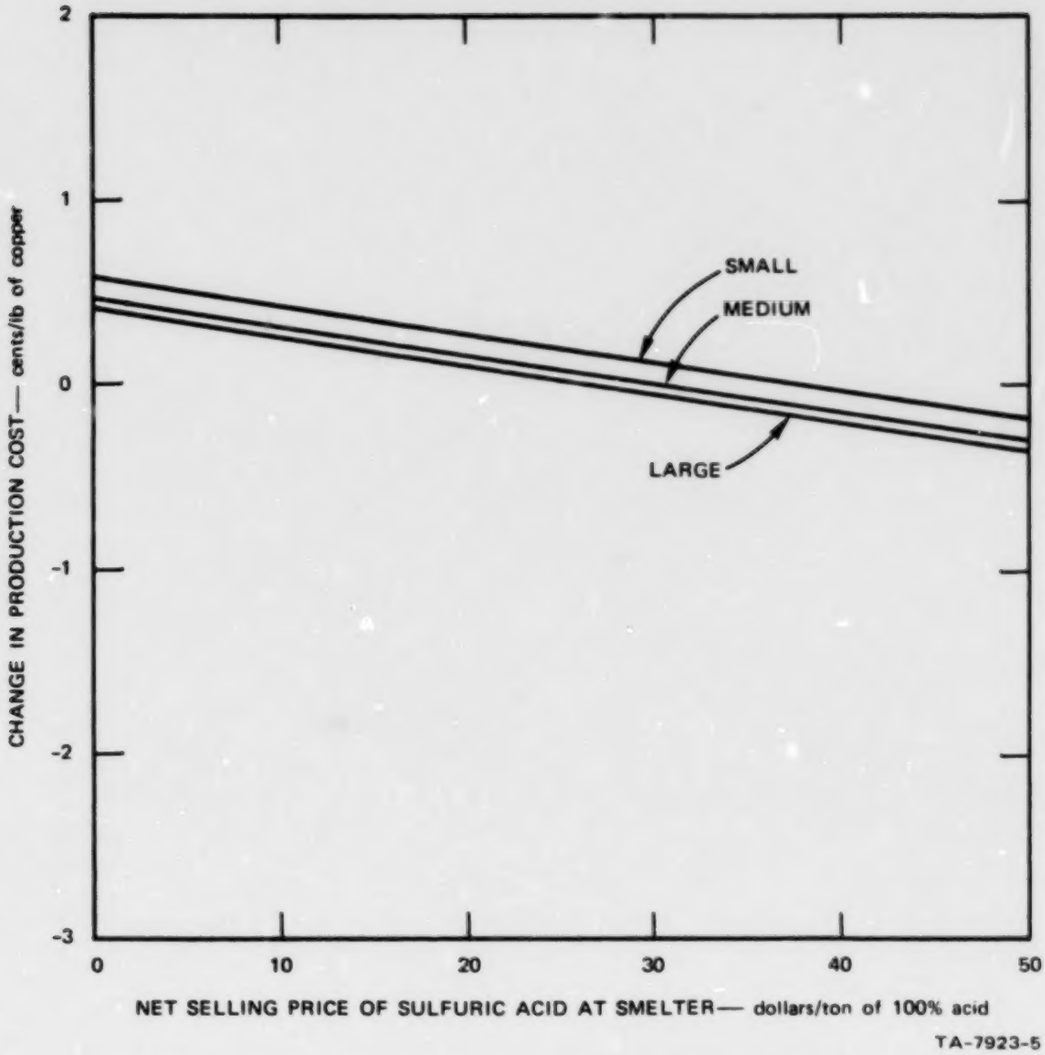

FIGURE 5 MODEL B COPPER SMELTERS: CAT-OX SYSTEMS ON REVERBERATORY FURNACES—EFFECT ON COPPER PRODUCTION COSTS

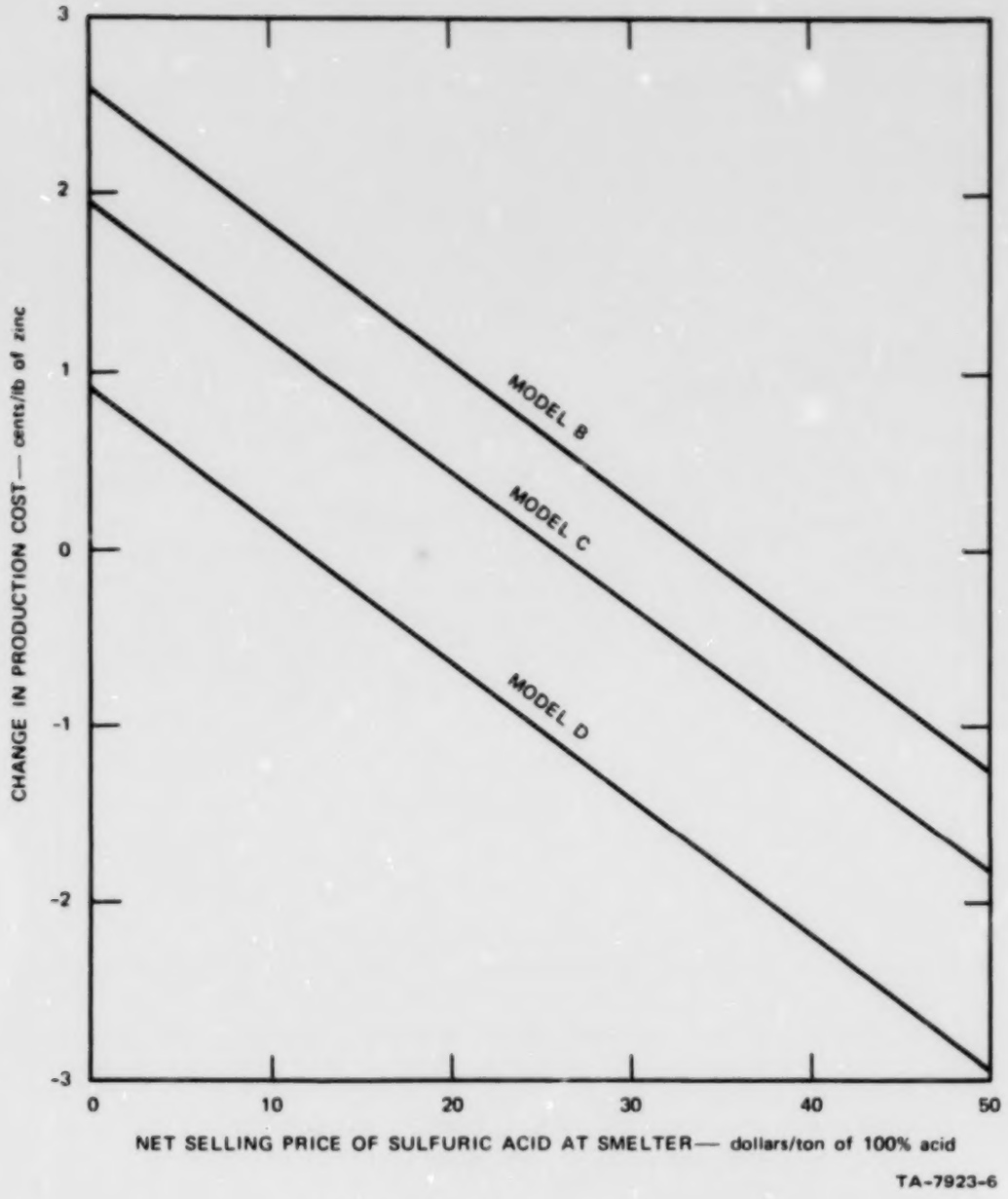

FIGURE 6 MODEL ZINC SMELTERS B, C, AND D: EFFECTS OF CAT-OX SYSTEMS ON ZINC PRODUCTION COSTS

VII GENERAL DISCUSSION

A. Evaluation of the Cat-Ox System

There are no reasons to doubt the technical feasibility of the basic Cat-Ox process. As is noted above, the basic process (essentially, the contact process) is fully established. The version of the Cat-Ox system proposed for application to smelters need not be seriously limited by the types of problems encountered in power plant applications (see Part III of Final Report for this study).

There are three principal technical problems (actual or potential) in the Cat-Ox process; these are listed below in their order of importance:

1. Dust collection
2. Acid mist formation and collection
3. Corrosion.

Of these three, corrosion is dealt with most readily. It presents its greatest threat in heat exchangers, where it can be avoided, but only at the expense of reduced heat recovery and of increased capital and operating costs. Dust collection is potentially by far the greatest problem, one which is apparently not yet fully resolved in the Cat-Ox systems designed for power plant applications. However, in the case of smelter gas Cat-Ox plants, where the feed gas is to be cleaned by well established methods, dust should not present any problems that cannot be anticipated fully on the basis of experience with standard contact plants. It should be possible to build a Cat-Ox plant for such service with reasonable confidence by using experience gained in the design of conventional acid plants.

Acid mist collection presents at least a potential problem primarily because of its interrelationship with the dust collection problem. Collection of the acid mist itself is not likely to present any serious

problems, since fibrous mist eliminators of the Brink type[1] have been amply demonstrated to give both high efficiency and reliability in mist collection. On the other hand, if there are solid particles in the gas stream, they will tend to plug the fiber bed. However, with gas of the cleanliness specified in this study, the rate of solids buildup in the mist eliminator will probably be sufficiently low that no unreasonable amount of maintenance will be required.

The Cat-Ox system is appropriate only for use on relatively dilute gases (those containing about 2 percent or less of sulfur dioxide). For operation on richer gases, it has no obvious advantages over the standard contact process. Without detailed comparative analysis, it is not possible to determine at what (low) sulfur dioxide concentration level in smelter gas the Cat-Ox process would begin to show a net economic advantage over the conventional contact process in which the feed gas is dehumidified and then dried before it enters the converter. The conventional process should avoid the potential corrosion problems associated with direct conversion of the wet gas. Auxiliary heat will be required at sulfur dioxide concentrations below a minimum of about 3.5 percent,[4] but more of the heat used can be recovered by exchange because the danger of reaching the acid dew point temperature will be eliminated, and less heat will be consumed in concentrating the acid produced. On the other hand, additional energy must be consumed in refrigeration in order to dehumidify the feed gas and maintain the water balance necessary to produce concentrated acid. At sulfur dioxide concentrations under 2 percent, it will become progressively less practical to employ the refrigeration necessary to permit production of acid as strong as 93 percent.[3]

In Table VI the summarized capital and operating costs of alternative Cat-Ox and contact process plants are presented for Zinc Smelter Model D, where the concentration of sulfur dioxide in the gas is 2.0 percent. The capital and operating costs for the contact process plant include allowances for use of auxiliary heat and of refrigeration of the cooling water, and were drawn from Reference 9. The indicated costs show a

Table VI

COMPARISON OF COSTS OF ALTERNATIVE CAT-OX AND CONTACT PROCESS PLANTS FOR ZINC SMELTER MODEL D

Control System	Cat-Ox Plant[1]	Contact Process Plant[2,3]
Capital Cost ($)	6,815,000	9,800,000
Annual Cost ($)	2,089,000	2,700,000
Production Cost of 93-percent Acid ($/ton 100% acid)	11.75	15.20

[1] Includes gas cleaning system.

[2] Includes auxiliary gas heater and refrigeration system for cooling water.

[3] Data from Reference 9.

substantial saving for the Cat-Ox system, although -- in view of the probable precision of the estimates -- the actual cost differences might not necessarily be as large as estimated. Presumably, the comparison should increasingly favor the Cat-Ox system as the sulfur dioxide concentration in the gas is reduced below 2.0 percent.

The most severe apparent limitations on the application of the Cat-Ox process to smelter gases are economic rather than technical. The costs of recovering sulfur by-products from dilute gases are inherently high, and this affects not only the Cat-Ox process but all alternative recovery processes. A specific limitation on the Cat-Ox process is that its product is sulfuric acid. As is discussed below, the geographical areas of the United States in which there is the greatest potential application of the Cat-Ox process are those in which there are only limited markets for the acid.

B. Disposal of By-Products

The sizes and availabilities of markets for sulfur by-products producible at smelters have been presented in the McKee report,[9] in which estimated by-product prices were based on an assumed Gulf Coast sulfur price of $30/long ton, f.o.b. At the time of the previous study[9] it was estimated that the price of $30 was a likely average for the period up to 1975. However, sulfur supplies have since shifted from shortages to surpluses in a period of only about a year, and sulfur prices have become chaotic. The development of sulfur surpluses has followed a continuing period of low activity in the market for fertilizers, which provides the largest outlet for sulfur.

In the next five years the withdrawal of marginal producers and a possible revival of the fertilizer market may cause sulfur prices to rise from their present lows. However, the figure of $30/long ton now appears to be an optimistic one. It perhaps represents the upper end of the probable range of Gulf Coast prices to be encountered in the period to 1975. It cannot even be assumed that the Gulf Coast sulfur price will continue to maintain its previous status as the base line for world sulfur prices. Nevertheless, if the above limitations are recognized, the assumption of the $30/long ton price is probably as good as any that can be made at this time. The estimates of sulfur by-product prices in smelter areas that are presented in Reference 9 can therefore be used as a first approximation if it is understood that they probably represent the most favorable situation that can be anticipated.

Most of the U.S. smelter units to which the Cat-Ox process might be applied are located in two regions, one comprised of Idaho and Montana, and the other of Arizona, New Mexico, and western Texas. In neither of these regions are there sufficient markets -- current or foreseeable -- to absorb all of the sulfuric acid potentially producible from smelter gases.[9] The amount of sulfuric acid needed can be produced more economically from available rich gases than it can be from dilute gases by

the Cat-Ox process or any other process for treating such gases. Local conditions at some specific smelters may make the Cat-Ox process a desirable one for treating the weak gases, even though probably not economic in the conventional sense. Net selling prices for acid at the smelters may frequently be $4/ton or less even for the quantities of acid that can be sold at all.

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REFERENCES

1. Brink, J. A., Jr., W. F. Burggrabe, and L. E. Greenwell, Mist Eliminators for Sulfuric Acid Plants, Chem. Eng. Progr. 64 (11), 82-86 (Nov. 1968)

2. Carter, B. M., Sulfuric Acid, Kirk-Othmer Encyclopedia of Chemical Technology, 1st Ed., 13, 458-501 (1954)

3. Donovan, J. R., and P. J. Stuber, Sulfuric Acid Production from Ore Roaster Gases, J. Metals 19 (11), 45-50 (Nov. 1967)

4. Duecker, W. W., and J. K. West (Eds.), "The Manufacture of Sulfuric Acid," Reinhold Publishing Co., New York (1959)

5. Guyot, G., SNPA Process for the Treatment of Residual Gases with Low Sulfur Dioxide Concentration, Chim. Ind., Génie Chim. 101 (1), 31-34 (Jan. 1969)

6. Guyot, G., Production of Concentrated Sulfuric Acid from Sulfur-Containing Gases with High Water Vapor Content, Chim. Ind., Génie Chim. 101 (6), 813-816 (Mar. 1969)

7. Guyot, G., and J. P. Zwilling, SNPA's Process for H_2SO_4 Production Developed with Eye on Air Pollution, Oil Gas J. 64 (47), 198-200 (Nov. 21, 1966)

8. Heinrich, R. F., and J. R. Anderson, Electro-Precipitation, in Cremer and Davies, "Chemical Engineering Practice," Vol. 3, pp. 484-534, Butterworths, London (1956)

9. McKee & Company, Arthur G., Systems Study for Control of Emissions -- Primary Nonferrous Smelting Industry, Final Report to National Air Pollution Control Administration, June 1969, Contract No. PH 86-68-85.

10. Monsanto Company, St. Louis, Missouri, Air Pollution Control for Electric Utilities, Bulletin (Undated -- issued 1970)

11. Monsanto Enviro-Chem Systems, Inc., St. Louis, Missouri, Cat-Ox System for Existing Power Generating Stations, Bulletin (Undated -- issued 1970)

12. Napier, D. H., and M. H. Stone, Catalytic Oxidation of Sulfur Dioxide at Low Concentrations, J. Appl. Chem. 8 (12), 781-786 (Dec. 1958)

13. Stites, J. G., Jr., W. R. Horlacher, Jr., J. L. Bachofer, Jr., and J. S. Bartman, Removing SO_2 from Flue Gas, Chem. Eng. Progr. 65 (10), 74-79 (Oct. 1969)

14. Tigges, A. J., Recovery of Values from Sulfur-Dioxide-Containing Flue Gases, Brit. Pat. No. 1,074,937 (July 5, 1967)

15. Zawadzki, E. A., Removal of Sulfur Dioxide from Flue Gases: The BCR Catalytic Gas Phase Oxidation Process, Trans. Soc. Mining Engrs. AIME 232, 241-246 (Sept. 1965)

Appendix A

SMELTER MODELS

The models of hypothetical copper, lead, and zinc smelters were created by Arthur G. McKee & Company, and are described in full in the McKee report.[A2] The essential features of the models directly pertinent to the present study are summarized here. Some additional model conditions, specific to the present study, were set by SRI, as indicated below.

In Table A-1 are presented the data on gas stream compositions, gas flow rates, and sulfur emissions for each of the model smelters. The data on metal production at the model smelters are given in Table A-2. The remainder of the model conditions are summarized below. Conditions specified by SRI are noted by an asterisk.

A. Plant Operating Time

330 days/year

24 hours/day

B. Gas Cleaning

1. Gases are assumed to have been cleaned in a hot electrostatic precipitator to a residual dust and fume content of 0.1 grain/std cu ft. The cost of hot, dry gas cleaning is not charged against sulfur oxides recovery.

*2. The gas leaving the hot precipitator is assumed to be cleaned in a system typical of those used for cleaning feed gases to a contact sulfuric acid plant[A1] (see Appendix C). The costs (capital and operating) of this secondary cleaning system are charged against sulfur oxides recovery. The cleaned gas is assumed to be at 110°F and essentially 1 atm pressure, and to be saturated with water vapor. It is further assumed that the residual concentrations of impurities are at least as low as those Donovan and Stuber[A1] have specified to be acceptable in contact sulfuric acid plants:

Table A-1

SMELTER MODELS
SUMMARY OF GAS COMPOSITIONS AND FLOW RATES AND OF SULFUR EMISSIONS

Plant	Model	Process Unit	Gas Temp. (°F)	Gas Composition (%)				Gas Flow Rate 1,000 SCFM (32°F, 1 atm)			Sulfur Equivalent (short tons/day)		
				SO_2	SO_3	O_2	H_2O	Small	Medium	Large	Small	Medium	Large
Copper	A	Reverberatory Furnace	550	1.89		6.48	11.7	69.9	139.8	209.7	84.6	169.2	253.8
		Converters	645	3.82				64.8 [1]	129.6 [2]	194.4 [2]	158.9	317.8	476.7
	B	Roaster	550	8.00		5.71	34.8	36.0	72.0	108	183.8	367.6	551.4
		Reverberatory Furnace	550	0.91				42.15	84.3	126.5	24.6	49.2	73.8
		Converters	637	3.78		16.1		58.04 [3]	116.1 [4]	174.1 [4]	141.6	283.2	424.8
Zinc	A	Roaster	600	7.1	0.1	10.9	0.05	19.31	38.62	57.93	89.6	179.2	268.8
		Sinter plant	500	0.048	0.0016	18.0	3.2	29.8	59.6	89.4	0.9	1.8	2.7
	B	Roaster	600	0.9		18.0		133.2	--	--	77.1	--	--
		Sinter plant	300	0.5		18.0		47.9	--	--	15.4	--	--
	C	Roaster	400	0.8		16.0		--	353.4	--	--	181.8	--
	D	Sinter-Roaster	300	2.0		16.0		--	144.0	--	--	185.2	--
Lead	A	Sinter plant	400	5.0	0.29	12.0		10.67	21.34	42.68	34.3	68.6	137.2

[1] Size recovery plant for 137% of average flow.
[2] Size recovery plant for 130% of average flow.
[3] Size recovery plant for 130% of average flow if gases combined with roaster gases.
[4] Size recovery plant for 123% of average flow if gases combined with roaster gases.

Table A-2

METAL PRODUCTION BY MODEL SMELTERS

Metal	Model	Size	Metal Production tons/day	Metal Production tons/year
Copper	A	Small	230	75,900
		Medium	460	152,000
		Large	690	228,000
	B	Small	230	75,900
		Medium	460	152,000
		Large	690	228,000
Zinc	A	Small	171.4	56,600
		Medium	342.8	113,000
		Large	514.2	170,000
	B	Small	171.4	56,600
	C	Medium	342.8	113,000
	D	Medium	342.8	113,000
Lead	A	Small	142.9	47,200
		Medium	285.8	94,300
		Large	571.6	189,000

Contaminant	Concentration, grains/std cu ft, dry basis
Chlorides (as Cl)	0.0005
Fluorides (as F)	0.0001
Arsenic (as As_2O_3)	0.0005
Lead (as Pb)	0.0005
Mercury (as Hg)	0.0001
Selenium (as Se)	0.022
H_2SO_4 mist (100%)	0.022
Total Solids (dust)	0.0005

*C. Sulfur Dioxide Collection Efficiency

The performance of the primary sulfur dioxide collection system is to be as follows, defined in terms of collection efficiency or of sulfur dioxide concentration in the exit gas:

SO_2 Concentration in Feed Gas (%)	Efficiency (%) or Concentration in Exit Gas (ppm)
Under 1.0	500 ppm
1.0 to 2.0	95%
Over 2.0	98%

In cases where sulfur dioxide is concentrated for conversion to another product in a secondary process, the efficiency of the conversion step is to be taken as a reasonable one for the process assumed.

*D. Cooling Water

The capital and operating costs of the sulfur dioxide control system are to include the costs of a water cooling tower. Cooling water costs will be for makeup only.

References

A1. Donovan, J. R., and P. J. Stuber, Sulfuric Acid Production from Ore Roaster Gases, J. Metals 19 (11), 45-50 (Nov. 1967)

A2. McKee & Company, Arthur, G., Systems Study for Control of Emissions -- Primary Nonferrous Smelting Industry, Final Report to National Air Pollution Control Administration, June 1969, Contract No. PH 86-68-85.

Appendix B

FACTORS AND CONDITIONS ASSUMED IN ESTIMATING CONTROL SYSTEM COSTS

The following conditions and cost factors were taken from the report by Arthur G. McKee & Company,[B1] except that the items marked with an asterisk are additional conditions specified by SRI.

A. Capital Costs

1. Capital costs do not include:

   (a) Working capital
   (b) Contingencies
   (c) Cost of land
   (d) Inventory
   (e) Interest on investment
   (f) Offsite utilities
   (g) Steam generators
   (h) Plant access
   (i) Cost of dry, hot gas cleaning

2. The cost of the wet cleaning system for the gas is charged to sulfur oxides control, but is estimated as a separate item (see Appendix C).

B. Depreciation

15-year, straight-line.

C. Direct Operating Costs (except utilities)

1.	Labor	$3.75/man-hour
2.	Supervision	4.75/man-hour
3.	Payroll benefits	25% of labor + supervision
4.	Maintenance materials	3% of capital cost of plant
5.	Factory supplies	0.5% of capital cost of plant

D. Indirect Costs

1. Controllable indirect costs (maintenance labor, laboratory, overhead, and supervision)

   50% of labor + supervision + maintenance materials

2. Noncontrollable indirect costs (local taxes and insurance)

   3% of capital cost of plant

E. Utilities

1.	Electrical power	1¢/kwh
2.	Steam	80¢/1000 lb *(400 psig, 750°F)
3.	Natural gas	40¢/million Btu
4.	Water	
	(a) Makeup cooling water	2¢/1000 gal
	(b) Process water	20¢/1000 gal
	*(c) Boiler feed water	40¢/1000 gal
	*(d) Retreatment of process steam condensates for boiler use	38¢/1000 gal
	*(e) Cooling water temperature	80°F

F. Waste Acid Disposal

(Weak, waste acid from preliminary gas cooling and cleaning.)
Cost of weak acid disposal 50¢/1000 gal

G. Plant Operating Time

330 days/year
24 hours/day

Reference

B1. McKee & Company, Arthur G., Systems Study for Control of Emissions -- Primary Nonferrous Smelting Industry, Final Report to National Air Pollution Control Administration, June 1969, Contract No. PH 86-68-85.

Appendix C

GAS CLEANING SYSTEM

The flowsheet for the gas cleaning system (Fig. C-1) was adapted from that portrayed for contact sulfuric acid plants in the Arthur G. McKee & Company final report.[C2] The inlet gas conditions were also assumed to be the same as those specified in the McKee report, except that a single, average value was taken for the SO_3 concentration (0.2% by volume). Under the conditions assumed, the water vapor condensed from the incoming gas is sufficient to balance the outflow of weak acid waste, so that no makeup scrubbing water is required. The cooling water used in the heat exchanger to cool the recirculated scrubbing water is assumed to be itself cooled in a water cooling tower. The water cooling tower is not shown in the flowsheet but is assumed to be part of the system. It is treated as a separate unit for convenience in cost accounting, even though the same water cooling tower would probably in most cases handle the cooling water for both the gas cleaning and the sulfur dioxide recovery systems.

The capital cost for the gas cleaning system (not including water cooling tower) was taken from the paper by J. M. Connor.[C1] Data points were taken from cost curve No. 2 of Connor's Fig. 5, corresponding to indirect cooling with a $30^{o}F$ approach between the cold gas and cooling water temperatures. The system capacity was converted from the original basis (tons per day of 100% H_2SO_4 with gas containing 8% SO_2) to the basis of volumetric gas flow at system exit conditions ($110^{o}F$, 1 atm, sat'd).

Connor's estimates were presumably made for the type of gas cleaning system illustrated in his paper, a scrubber-cooler followed by an indirect tubular type of gas cooler, with an electrostatic mist precipitator for final cleanup. Although the scrubbing and cooling equipment may therefore be different from that assumed in the present case, Connor's cost estimates (which were admittedly approximate) were taken to be sufficiently precise

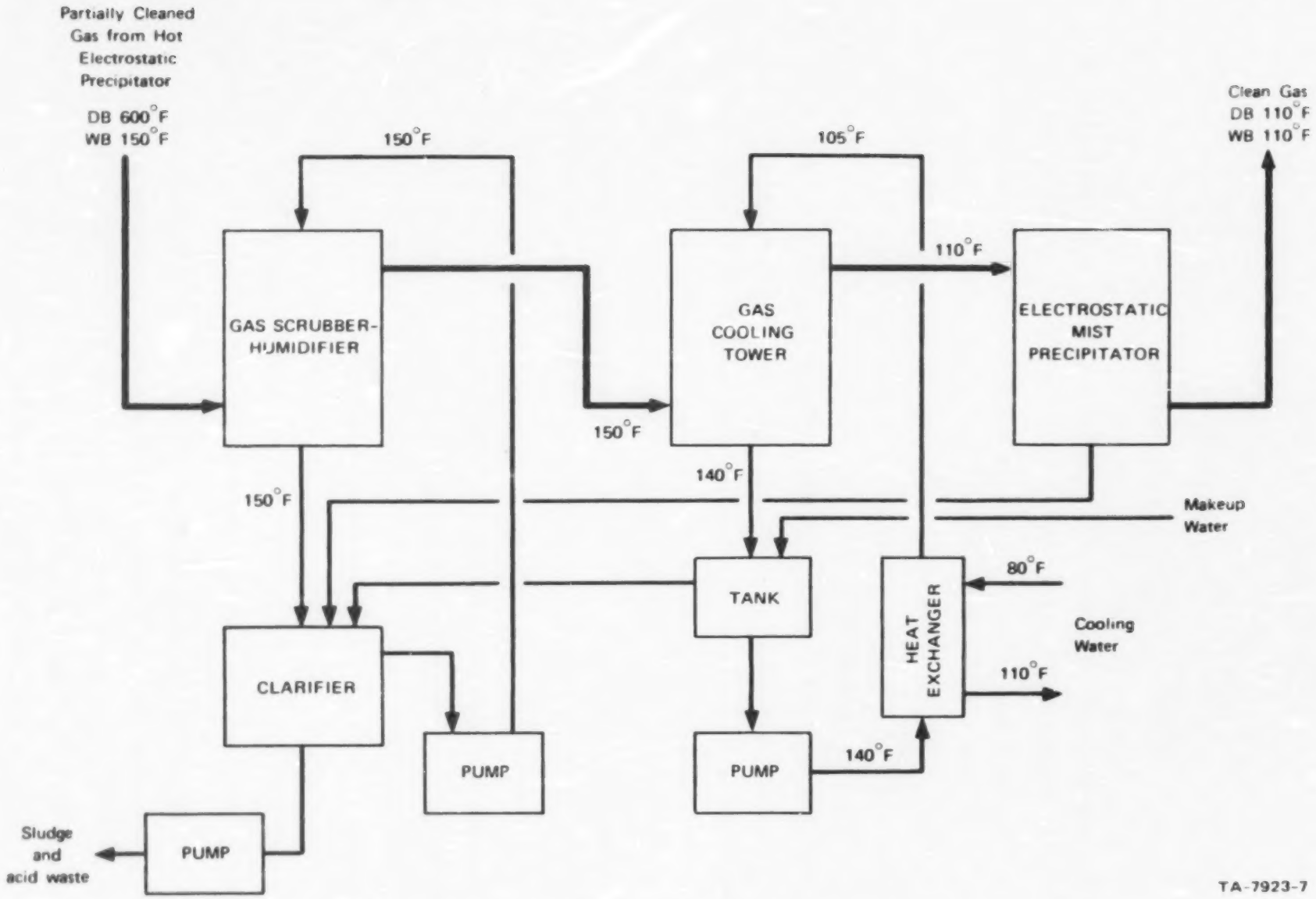

FIGURE C-1 GAS CLEANING SYSTEM FOR SMELTER GASES

for use in this analysis.

Connor's curves did not extend beyond a capacity equivalent to about 100,000 CFM of gas, but the plotted curve (Fig. C-2) was extrapolated arbitrarily to 1,000,000 CFM. The actual upper limit of validity probably corresponds to no more than 300 to 400,000 CFM. Above this size range, the use of multiple units of equipment may make the cost more nearly proportional to the first power of gas flow rate. However, none of the individual gas flows in the smelter models exceeds about 400,000 CFM, above which the curve in Fig. C-2 is shown as a broken line.

To obtain the curve of capital costs (Fig. C-2) for use in the present study, the capital cost of a water cooling tower was added to the cost of the remainder of the system as adapted from Connor's data.

The gas and water flows through the system were determined by making heat and material balances based on the conditions shown in Fig. C-1. Power requirements were estimated from literature data in a few instances, and calculated from guesstimates of gas pressure drop and pump heads in the rest. Utilities, labor requirements, and cost factors employed are summarized in Tables C-1 and C-2. The standard cost factors used were the same as those employed elsewhere in the study (Appendix B).

The total annual costs were calculated for five gas flow capacities ranging from 10,000 to 1,000,000 CFM (see Table C-3), using the data of Fig. C-2 and Tables C-1 and C-2, and were used to prepare the curve of annual cost, Fig. C-3. The curve probably is not valid for capacities greater than 300 to 400,000 CFM, and is shown as a broken line above the latter level.

References

C1. Connor, J. M., Economics of Sulfuric Acid Manufacture, Chem. Eng. Progr. 64 (11), 59-65 (Nov. 1968)

C2. McKee & Company, Arthur G., Systems Study for Control of Emissions -- Primary Nonferrous Smelting Industry, Final Report to National Air Pollution Control Administration, June 1969, Contract No. PH 86-68-85.

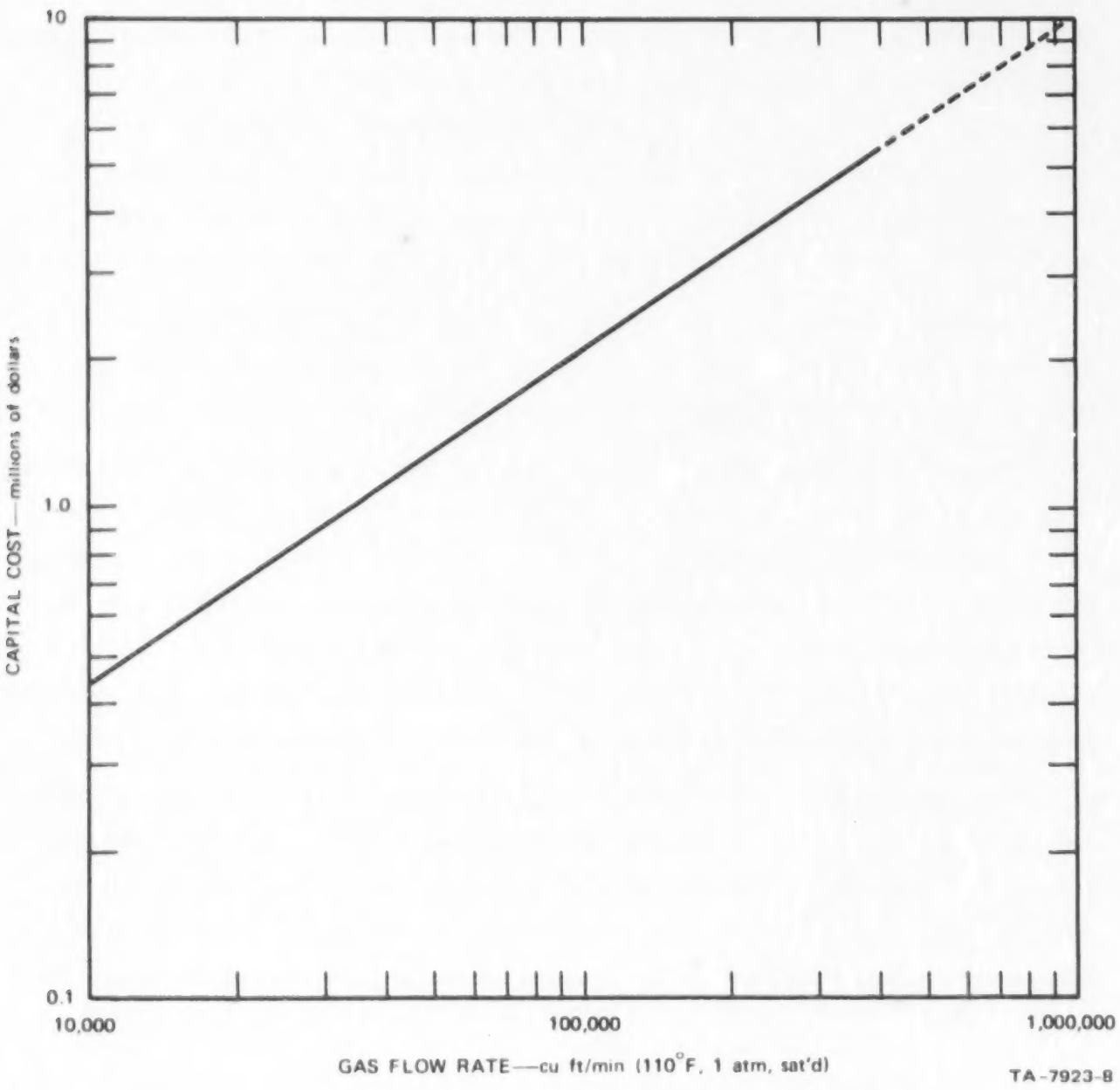

FIGURE C-2 CAPITAL COST OF GAS CLEANING SYSTEM FOR SMELTER GASES

Table C-1

GAS CLEANING SYSTEM FOR SMELTER GAS
LIQUID FLOWS AND POWER REQUIREMENTS

Item	Basis Gas Flow = 1000 CFM at 110°F, 1 atm, sat'd	
	Liquid Flow	Power
Gas Flow through System Δp = 14 in. w.c.		3.50 hp
Scrubber-Humidifier Circulated water	7.86 gpm	0.43 hp
Gas Cooling Tower Circulated water	35.7 gpm	1.50 hp
Cooling Water Circulation	41.7 gpm	1.40 hp
Waste Acid (21% H_2SO_4)	0.212 gpm	0.06 hp
Water Cooling Tower Circulated water Makeup water	41.7 gpm 4.17 gpm	1.91 hp
Subtotal		8.80 hp 6.57 kw
Electrostatic Precipitator		1.50 kw
Total		8.07 kw

Table C-2

GAS CLEANING SYSTEM FOR SMELTER GASES
UTILITIES AND OPERATING LABOR REQUIREMENTS

Item	Unit Cost	Utilities Basis:[1] Gas Flow = 1000 CFM @ 110°F, 1 atm, sat'd	
		Quantity	Annual Cost ($)
Electrical Power	$0.01/kwh		
Gas flow only		2.62 kw	207.50
Total		8.07 kw	639.14
Makeup Cooling Water	$0.02/1000 gal	4.17 gpm	39.63
Waste Acid Treatment	$0.50/1000 gal	0.212 gpm	50.37
Operating Labor	$3.75/hr	12 hrs/day[1]	14,850[1]
Supervision	$4.75/hr	2 hrs/day[1]	3,135[1]
Payroll Benefits	25% of Labor + Supervision		4,496[1]

Plant operating time = 330 days = 7920 hrs/yr.

[1]Labor costs are total for plant regardless of size.

Table C-3

GAS CLEANING SYSTEM FOR SMELTER GASES
CAPITAL AND TOTAL ANNUAL COSTS

Item	Cost Basis	Gas Flow Rate-CFM at 110°F, 1 atm, saturated				
		10,000	30,000	100,000	300,000	1,000,000
Capital Investment	$	436,000	930,000	2,104,000	4,480,000	10,156,000
	$/CFM	43.60	31.00	21.04	14.93	10.16
Annual Cost	$/yr					
A. Depreciation		29,100	62,000	140,200	298,670	677,100
B. Direct Operating Cost						
1. Labor		14,850	14,850	14,850	14,850	14,850
2. Supervision		3,135	3,135	3,135	3,135	3,135
3. Payroll benefits		4,496	4,496	4,496	4,496	4,496
4. Maintenance Materials		13,080	27,900	63,120	134,400	304,680
5. Factory supplies		2,180	4,650	10,520	22,400	50,780
6. Electricity		6,390	19,170	63,910	191,740	639,140
7. Makeup water		396	1,190	3,960	11,890	39,630
8. Waste acid treatment		504	1,510	5,040	15,110	50,370
C. Indirect Costs						
1. Controllable		15,530	22,940	40,550	76,190	161,330
2. Noncontrollable		13,080	27,900	63,120	134,400	304,680
Total Annual Cost	$/yr	102,741	189,741	412,901	907,281	2,250,191
	$/yr per CFM	10.27	6.33	4.13	3.02	2.25

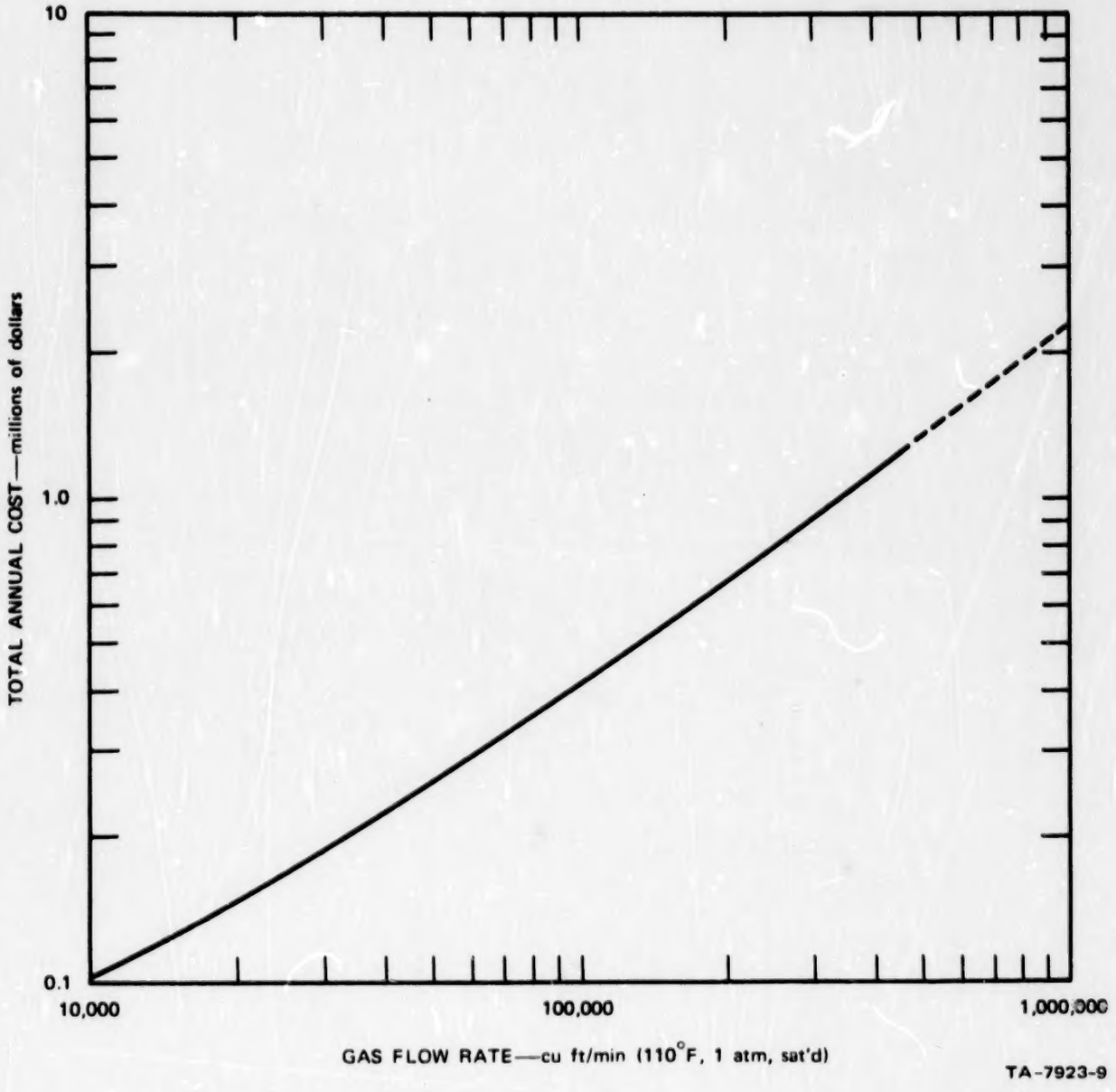

FIGURE C-3 TOTAL ANNUAL COST OF GAS CLEANING SYSTEM FOR SMELTER GASES